

# Controlling the pathways in “frustrated” ionization of strongly-driven $H_2$ with elliptical laser fields

H. Price, C. Lazarou, and A. Emmanouilidou  
*Department of Physics and Astronomy,  
 University College London, Gower Street,  
 London WC1E 6BT, United Kingdom*

(Dated: March 28, 2014)

The formation of highly excited neutral atoms during the break-up of strongly-driven molecules is a significant phenomenon. Past work has shown that during the formation of highly excited neutral atoms ( $H^*$ ) during the break-up of  $H_2$  in a linear laser field the electron that escapes does so either very quickly or after remaining bound for a few periods of the laser field. Here, we offer a physical picture of the electron-nuclear dynamics in  $H^*$  formation in elliptical laser fields, through Coulomb explosion. We show that with increasing ellipticity two-electron effects are effectively “switched-off”. Moreover, we identify the site the initially bound electron tunnels from and show how this tunneling site changes with ellipticity.

PACS numbers: 33.80.Rv, 34.80.Gs, 42.50.Hz

A wealth of physical phenomena take place during the fragmentation of strongly-driven molecules by intense infrared laser fields. Such phenomena include bond-softening and above-threshold dissociation [1, 2], molecular non-sequential double ionization (NSDI) [3–6] and enhanced ionization (EI) [6–8]. Exploring the inter-play of electronic and nuclear motion during the break-up of strongly-driven molecules is a task of great interest. Understanding break-up dynamics paves the way for controlling and imaging molecular processes [9]; it is, however, a highly challenging task due to the many degrees of freedom involved.

The formation of highly excited neutral fragments in linearly polarized laser fields has attracted a lot of interest in the last few years [10–14]. In [15] we reported a theoretical study of the mechanisms of this “frustrated”—since only one electron eventually escapes—double ionization process. The break-up of  $H_2$  into a proton, a Rydberg atom ( $H^*$ ) and an escaping electron through Coulomb explosion of the nuclei is a significant phenomenon. It accounts roughly for 10% of all possible events during the break-up of  $H_2$ . Thus, to obtain a complete picture of the break-up of  $H_2$  it is important to also understand the dynamics leading to  $H^*$  formation. For linear fields, we have shown that  $H^*$  formation takes place through two distinctly different routes depending on which one of the two ionization steps is “frustrated”. However,  $H^*$  formation in elliptical fields has not yet been addressed.

In this Letter, we aim to elucidate a challenging problem, namely, the electron dynamics and its inter-play with nuclear motion in  $H^*$  formation during the break-up of  $H_2$  by elliptical fields. We show that using the degree of ellipticity of the laser field we can control the pathways of  $H^*$  formation. Specifically, we show that using an elliptical field we can “switch-off” the contribution of the

pathway where two-electron effects are important (pathway B). We find that one-electron effects (pathway A) prevail with increasing ellipticity. Moreover, to explain why  $H^*$  formation decreases with ellipticity we identify the tunneling site of the initially bound electron (electron 2). To do so, at the time of tunnel ionization, we consider the combined potential of electron 2 in the presence of the laser field and the two-centre molecular ion. We check whether along the field direction—tunneling direction—this combined potential has a single or a double-well. In the double-well the potential of the electron is higher in one well (up-field) compared to the other well (low-field). We compute the percentage for electron 2 to tunnel ionize from a single-well, up-field well or a low-field one and investigate how these percentages change with ellipticity.

Currently, quantum mechanical computations in 3-dimensions for  $H^*$  formation during the break-up of strongly-driven  $H_2$  are out of reach. In this work, we present a 3-dimensional semiclassical study of  $H^*$  formation in elliptically polarized laser fields. We do so by fully accounting for two-electron effects as well as nuclear and electronic motion at the same time. Previous semiclassical 3-d models did not account for nuclear motion; they used fixed-centers to elucidate double ionization in strongly-driven diatomic molecules [16–18]. In our study of  $H^*$  formation during the break-up of  $H_2$  in a linear laser field [15] we fully accounted for nuclear motion; our results were in agreement with experimental ones [10]. Let us briefly outline the steps our semiclassical 3-d model entails, for details see [15]. First, we set up the initial electronic phase space distribution. We consider an elliptically polarized laser field with its  $\hat{z}$  axis parallel to the molecular axis. The field is taken to be  $\vec{E}(t) = E_0(t)(\cos(\omega t)\hat{z} + \epsilon \sin(\omega t)\hat{x})$  at 800 nm corresponding to  $\omega = 0.057$  a.u. (a.u. - atomic units) with  $\epsilon$  the ellipticity of the field. In our simulation the pulse en-

velope  $E_0(t)$  is defined as  $E_0(t) = E_0$  for  $0 < t < 10T$  and  $E_0(t) = E_0 \cos^2(\omega(t - 10T)/8)$  for  $10T < t < 12T$ , with  $T$  the period of the field. We start the time propagation at  $\omega t_0 = \phi_0$  where the phase of the laser field  $\phi_0$  is chosen randomly. In the current study we consider an intensity of  $1.5 \times 10^{14}$  W/cm<sup>2</sup> which is in the tunneling regime. That is, the instantaneous field strength at phase  $\phi_0$  is smaller than the threshold field strength for over-the-barrier ionization. We assume one electron (electron 1) tunnel ionizes, i.e., tunnels through the field-lowered Coulomb potential to the continuum with an initial velocity distribution that is perpendicular to the direction of the field [19]. The initially bound electron (electron 2) is described by a one-electron microcanonical distribution [20]. We use the tunneling rate provided in [21] with field strength the instantaneous one at  $\phi_0$ . We use 0.57 a.u. (1.28 a.u.) as the first (second) ionization potentials.

Second, we take the initial vibrational state of the nuclei to be the ground state ( $E_0 \approx 0.01$  a.u.) of a Morse potential and restrict the initial distance of the nuclei to  $R_0 = 1.4$  a.u. (equilibrium distance) [22]. We choose the Wigner distribution of the above state [23] to describe the initial state of the nuclei. Finally, we propagate the full four-body Hamiltonian in time, i.e., including both electronic and nuclear motion, using the Classical Trajectory Monte Carlo method [24]. During time propagation, we allow the initially bound electron to tunnel at the classical turning points along the field axis using the WKB approximation, for details see [25]. We finally select those trajectories leading to a break-up of  $H_2$  with  $H^+$ ,  $H^*$  (where  $*$  denotes an electron in a  $n > 1$  quantum state) and a free electron as fragments. We identify the electrons captured in a Rydberg  $n$  quantum state of  $H^*$  following the process outlined in [26].

We first investigate the dependence of the two pathways of  $H^*$  formation on the degree of ellipticity of the laser field. These pathways can be categorized as to which one of the two ionization steps, i.e., the earlier tunnel ionization of electron 1 or the later tunnel ionization of electron 2 is “frustrated” [15]. In Fig. 1 a) we show pathway A where electron 1 tunnel ionizes, subsequently escaping very quickly. Electron 2, later, tunnel ionizes and quivers in the laser field; however, when the field is turned off, electron 2 does not have enough drift energy to escape and occupies a Rydberg state of the H-atom instead. Hence, in Pathway A the later ionization step is “frustrated”. In Fig. 1 b) we show pathway B where electron 1 tunnel ionizes very quickly, quivering in the field, while electron 2 tunnel ionizes and escapes after a few periods of the laser field. When the laser field is turned off, electron 1 does not have enough energy to escape and remains in a Rydberg state of the H-atom instead, i.e., the earlier ionization step is “frustrated”.

In Fig. 2 we show how the probability of pathway A and B (out of all trajectories) changes with the degree of ellipticity of the laser field. We find that as  $\epsilon$  increases the

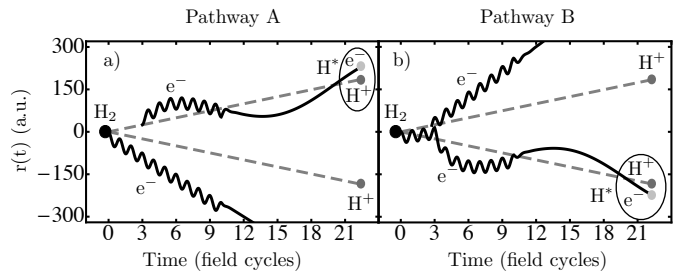


FIG. 1. (Color online) Schematic illustration of the two routes leading to formation of  $H^*$ : a) Pathway A, b) Pathway B. Shown is the time-dependent position along the laser field for electrons (black lines) and ions (gray broken lines). This figure appears in [15]; we also include it here for completeness.

probability of pathway B drops more sharply than that of A. For instance, for  $\epsilon = 0$  pathway B is 1.6 times more probable than pathway A, while for  $\epsilon = 0.45$  pathway B is roughly 6 times less probable than A. Thus, for  $\epsilon > 0.4$  pathway B is practically “switched-off” with pathway A prevailing.

The question that naturally arises is why pathway B is more sensitive to the ellipticity of the laser field. It is known that double ionization events where re-collisions prevail are very sensitive to  $\epsilon$  [27]. The reason is that a slight ellipticity of the laser field offsets the electron from the ion roughly by  $5\epsilon E/\omega^2$  making a re-collision less probable [28]. We find that the dependence on  $\epsilon$  of double ionization events, see [27], strongly resembles the dependence on  $\epsilon$  of our “frustrated” double ionization events shown in Fig. 2. Namely, we find that double ionization events where re-collisions/enhanced ionization prevail change with  $\epsilon$  in a similar way as the probability for pathway B/A does, respectively. This strongly suggests that two-electron effects in the form of re-collisions underly pathway B and not pathway A.

Indeed, in [15] we have provided evidence that one-electron effects prevail in pathway A, while two-electron effects prevail in pathway B. That is, we have shown that in pathway A electron 2 transitions from the ground state of the  $H_2$  molecule to a high Rydberg state of the H-atom by gaining energy through a strong interaction with the laser field. This gain of energy resembles enhanced ionization in  $H_2^+$  [7]. We have also provided evidence that in pathway B electron 2 gains energy to ionize mainly through two-electron effects resembling Delayed NSDI (non-sequential double ionization) which is a major pathway of double electron escape (also referred to as re-collision-induced excitation with subsequent field ionization, RESI [29]). In Delayed NSDI (weak re-collision) the re-colliding electron returns to the core close to a zero of the field, transfers energy to the second electron and one electron escapes with a delay after re-collision. For pathway B the electron-electron correlation is in the form of “frustrated” delayed NSDI since one electron eventu-

ally does not escape. From the above, it follows that the dependence of the probability of pathways A and B on  $\epsilon$  (Fig. 2) provides strong support that re-collisions underly pathway B.

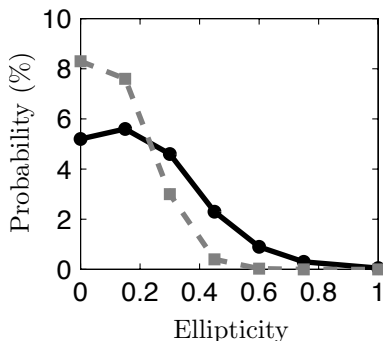


FIG. 2. (Color online) Probability (out of all trajectories) of pathway A (solid black line and circles) and pathway B (grey dashed line and squares) for formation of  $H^*$ .

Fig. 2 shows that two-electron effects are essentially “switched-off” in  $H^*$  formation for  $\epsilon > 0.4$  with pathway A prevailing. This prevalence of one-electron effects with increasing  $\epsilon$  is also evident in the observable momentum space of the escaping electron. In Fig. 3 we plot the total x-z momentum distribution of the escaping electron for ellipticities 0, 0.45, 0.75 and 1, with x-z the plane of the laser field. The total 2-d distributions account for both pathways and all initial tunneling directions of electron 1. For  $\epsilon = 0$  (Fig. 3 a)) the traces of both pathways A and B (Fig. 2) are present in the 2-d momentum distribution. The trace of pathway B is the large spread in momentum [15] which is mostly due to the strong interaction of electron 2 with the Coulomb potential [30]. However, for larger values of  $\epsilon$  this large spread disappears, see Fig. 3 b), c) and d); this is a clear signature of the prevalence of pathway A. In addition, for larger values of  $\epsilon$ , see Fig. 3 b) and c), we obtain an asymmetric two-lobe momentum distribution. This asymmetry, first observed in [31], has sparked a lot of studies in single ionization of atoms in elliptical fields. It has been, mainly, attributed to the effect of the Coulomb potential [32]. Since our 3-d semiclassical model fully accounts for the Coulomb potential the asymmetry in the momentum distribution is also evident in our results in Fig. 3 b) and c). However, besides the current study, studies of this asymmetry for molecular systems are few; they include a theoretical one of strongly-driven  $H_2^+$  [33] and an experimental one on double ionization of  $H_2$  [34]. Our results for  $H^*$  formation in Fig. 3 b) and c) show that with increasing  $\epsilon$  the two-lobe structure tends to align closer to the minor axis of the field (x-axis in our case) [33, 34]. Also, in Fig. 3 d) we show that even for a circular field there is an asymmetry in the 2-d momentum distribution. With one-electron effects (pathway A) prevailing for  $\epsilon = 1$ , the

observed asymmetry is due to the asymmetric Coulomb potential of the molecular ion.

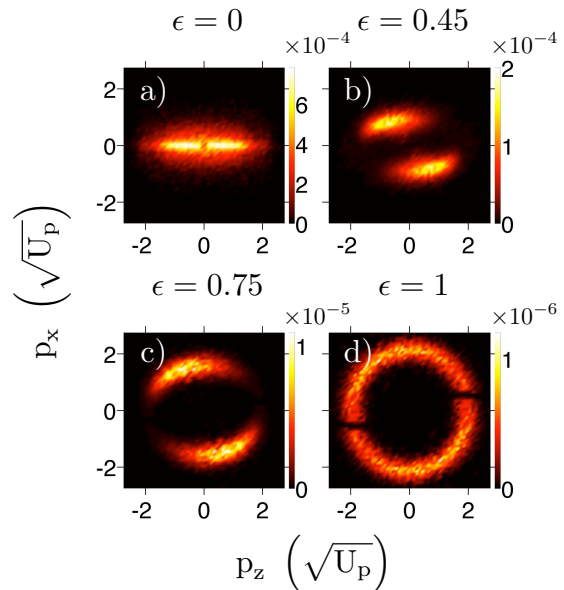


FIG. 3. (Color online) Total 2-d electron momentum distribution of the escaping electron expressed in  $\sqrt{U_p}$ ,  $U_p = E_0^2/4\omega^2$ , for  $\epsilon = 0$  a),  $\epsilon = 0.45$  b),  $\epsilon = 0.75$  c) and  $\epsilon = 1$  d).

Next, we address why the probability for  $H^*$  formation decreases with increasing degree of ellipticity of the field (Fig. 2). We do so by quantifying how the sites electron 2 tunnel ionizes from change with ellipticity. Specifically, we consider the combined potential of electron 2 in the presence of the two nuclei and the laser field along the direction of the laser field (tunneling direction). Our results indicate that when electron 2 tunnel ionizes the inter-nuclear distances range from intermediate to large. For these distances and at times close to extrema of the field we find that the potential of electron 2 along the direction of the field has either a double or a single-well. For the double-well an inner barrier is present such that the potential of electron 2 is higher in one well (up-field) compared to the other well (low-field) (as is the case for enhanced ionization [6–8]). The tunnel ionization sites are thus an up-field, low-field and a single-well.

In Fig. 4 we show the percentage out of all  $H^*$  formation events for electron 2 to tunnel ionize from these sites with increasing ellipticity. We emphasize that in Fig. 4 we show percentages out of all  $H^*$  formation events while in Fig. 2 we show probabilities out of all events. Thus, to obtain the probability out of all events, for instance, for tunneling through a single-well one has to multiply the corresponding percentage in Fig. 4 with the corresponding probability in Fig. 2. Our results account for both pathways A and B. We find that electron 2 tunnel ionizes from a single-well with a percentage that increases roughly from 9.5% to 41.5% as  $\epsilon$  increases from 0

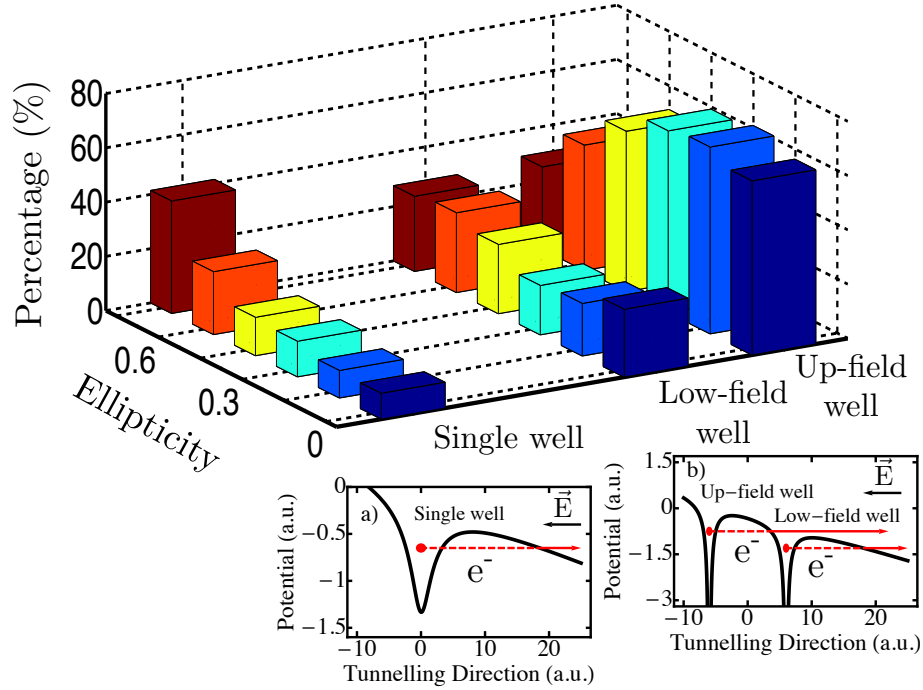


FIG. 4. (Color online) Percentage (out of all  $H^*$  formation events) for electron 2 to tunnel ionize from an up-field well, a low-field well and a single one as a function of  $\epsilon$ . The cartoons underneath the probability histogram illustrate electron tunneling from a single-well a) and an up-field and low-field well b); the potential is taken along the direction of the field.

to 0.75. This can be understood as follows: For small  $\epsilon$ , electron 2 tunnel ionizes mostly along the molecular axis or at small angles around it; the potential along these directions has mostly a double-well. However, for large  $\epsilon$  electron 2 tunnel ionizes at a larger range of angles around the molecular axis; the potential along a direction at a large angle from the molecular axis has mostly a single-well. While the percentage for tunneling through a single-well increases, the percentage for tunneling from an up-field well decreases from 64.2% to 30.4% as  $\epsilon$  increases from 0 to 0.75. But the probability for tunneling through an up-field well to the continuum is, in general, larger than through a single-well. It thus follows that the probability for  $H^*$  formation decreases with increasing  $\epsilon$ , see Fig. 2. We also find that when electron 2 tunnel ionizes the inter-nuclear distances are, on average, for  $\epsilon = 0$  equal to 4.9 a.u., 8.2 a.u. and 6.6 a.u. while for  $\epsilon = 0.6$  equal to 6.5 a.u., 8.2 a.u. and 9.7 a.u. for tunneling through an up-field, low-field and a single-well, respectively. Moreover, we find that electron 2 has a significant probability (25%) to tunnel ionize from the low-field well for all  $\epsilon$  considered. This is the case even for linear polarization which is rather interesting. That is, while our result refers to  $H^*$  formation, for enhanced ionization in a linear field it is known that tunneling occurs mainly from the up-field well. However, a recent quantum mechanical study of enhanced ionization seems to suggest

that tunneling through the low-field well also takes place [35].

In conclusion, in this work we offer a physical picture of the electronic and nuclear dynamics in  $H^*$  formation during the break-up of strongly-driven  $H_2$  by elliptical laser fields. This is an important but challenging phenomenon. We find that electron 2 tunnel ionizes for small ellipticities mostly from an up-field well at intermediate inter-nuclear distances while for large ellipticities mostly from a single-well at large inter-nuclear distances. This is consistent with the probability for  $H^*$  formation decreasing with ellipticity. Moreover, we find that with increasing ellipticity we “switch-off” two-electron effects. While doing so, the observable momentum space of the escaping electron clearly bears the imprints of one-electron effects. That is, we find that pathway A, which is similar to a “frustrated” enhanced ionization process, prevails with increasing ellipticity. Since enhanced ionization is only present in molecular systems, one would expect that for large ellipticity it might be easier to create excited neutral fragments from strongly-driven molecules than from strongly-driven atoms. Future studies could address the validity of this statement.

*Acknowledgments.* A.E. acknowledges support from EPSRC grants no. H0031771 and J0171831 and the use of the computational resources of Legion at UCL.

- 
- [1] A. Giusti-Suzor, X. He, O. Atabek, and F. H. Mies, *Phys. Rev. Lett.* **64**, 515 (1990).
- [2] A. Zavriyev, P. H. Bucksbaum, H. G. Muller, and D. W. Schumacher, *Phys. Rev. A* **42**, 5500 (1990).
- [3] A. Staudte, C. L. Cocke, M. H. Prior, A. Belkacem, C. Ray, H. W. Chong, T. E. Glover, R. W. Schoenlein, and U. Saalmann, *Phys. Rev. A* **65**, 020703(R) (2002).
- [4] H. Sakai, J. J. Larsen, I. Wendt-Larsen, J. Olesen, P. B. Corkum, and H. Stapelfeldt, *Phys. Rev. A* **67**, 063404 (2003).
- [5] A. S. Alnaser, T. Osipov, E. P. Benis, A. Wech, B. Shan, C. L. Cocke, X. M. Tong, and C. D. Lin, *Phys. Rev. Lett.* **91**, 163002 (2003).
- [6] H. Niikura, F. Légaré, R. Hasbani, A. D. Bandrauk, M. Yu. Ivanov, D. M. Villeneuve, and P. B. Corkum, *Nature* **417**, 917 (2002).
- [7] T. Zuo and A. D. Bandrauk, *Phys. Rev. A* **52**, R2511 (1995); T. Seideman, M. Yu. Ivanov, and P. B. Corkum, *Phys. Rev. Lett.* **75**, 2819 (1995); D. M. Villeneuve, M. Yu. Ivanov, and P. B. Corkum, *Phys. Rev. A* **54**, 736 (1996); E. Dehghanian, A. D. Bandrauk, and G. Lagmago Kamta, *ibid* **81**, 061403 (2010).
- [8] J. Wu, M. Meckel, L. Ph. H. Schmidt, M. Kunitski, S. Voss, H. Sann, H. Kim, T. Jahnke, A. Czasch, and R. Dörner, *Nature Comm.* **3** 1113 (2012).
- [9] M. Meckel, D. Comtois, D. Zeidler, A. Staudte, D. Pavičić, H. C. Bandulet, H. Pépin, J. C. Kieffer, R. Dörner, D. M. Villeneuve, and P. B. Corkum, *Science* **320**, 1478 (2008).
- [10] B. Manschwetus, T. Nubbemeyer, K. Gorling, G. Steinmeyer, U. Eichmann, H. Rottke, and W. Sandner, *Phys. Rev. Lett.* **102**, 113002 (2009).
- [11] T. Nubbemeyer, K. Gorling, A. Saenz, U. Eichmann, and W. Sandner, *Phys. Rev. Lett.* **101**, 233001 (2008).
- [12] T. Nubbemeyer, U. Eichmann, and W. Sandner, *J. Phys. B* **42**, 134010 (2009); B. Manschwetus, H. Rottke, G. Steinmeyer, L. Foucar, A. Czasch, H. Schmidt-Böcking, and W. Sandner, *Phys. Rev. A* **82**, 013413 (2010); B. Ulrich, A. Vredenburg, A. Malakzadeh, M. Meckel, K. Cole, M. Smolarski, Z. Chang, T. Jahnke, and R. Dörner, *Phys. Rev. A* **82**, 013412 (2010).
- [13] J. McKenna, A. M. Saylor, B. Gaire, N. G. Kling, B. D. Esry, K. D. Carnes, and I. Ben-Itzhak, *New Journal of Physics* **14**, 103029 (2012).
- [14] J. Wu, A. Vredenburg, B. Ullrich, L. Ph. H. Schmidt, M. Meckel, S. Voss, H. Sann, H. Kim, T. Jahnke, and R. Dörner, *Phys. Rev. Lett.* **107**, 043003 (2011).
- [15] A. Emmanouilidou, C. Lazarou, A. Staudte, and U. Eichmann, *Phys. Rev. A* **85**, 011402 (R) (2012).
- [16] J. Liu, D. F. Ye, J. Chen, and X. Liu, *Phys. Rev. Lett.* **99**, 013003 (2007).
- [17] D. F. Ye, J. Chen, and J. Liu, *Phys. Rev. A* **77**, 013403 (2008).
- [18] A. Emmanouilidou and A. Staudte, *Phys. Rev. A* **80**, 053415 (2009).
- [19] X. Hao, G. Wang, X. Jia, W. Li, J. Liu, and J. Chen, *Phys. Rev. A* **80**, 023408 (2009).
- [20] L. Meng, C. O. Reinhold, and R. E. Olson, *Phys. Rev. A* **40**, 3637 (1989).
- [21] R. Murray, M. Spanner, S. Patchkovskii, and M. Yu. Ivanov, *Phys. Rev. Lett.* **106**, 173001 (2011).
- [22] A. Saenz, *Phys. Rev. A* **61**, 051402 (R) (2000).
- [23] A. Frank, A. L. Rivera, and K. B. Wolf, *Phys. Rev. A* **61**, 054102 (2000).
- [24] R. Abrines, I. C. Percival, and N. A. Valentine, *Proc. Phys. Soc.* **89**, 515 (1966).
- [25] J. S. Cohen, *Phys. Rev. A* **64**, 043412 (2000); for the WKB transmission probability see Chapter 7 in Eugen Merzbacher, “Quantum Mechanics”, 1998.
- [26] R. L. Becker and A. D. MacKellar, *J. Phys. B* **17**, 3923 (1984).
- [27] H. Sakai, J. J. Larsen, I. W. Larsen, J. Olesen, P. B. Corkum, and H. Stapelfeldt, *Phys. Rev. A* **67**, 063404 (2003).
- [28] P. Dietrich, N. H. Burnett, M. Ivanov, and P. B. Corkum, *Phys. Rev. A* **50**, R3585 (1994).
- [29] R. Kopold, W. Becker, H. Rottke, and W. Sandner, *Phys. Rev. Lett.* **85**, 3781 (2000); B. Feuerstein, R. Moshhammer, D. Fischer, A. Dorn, C. D. Schröter, J. Deipenwisch, J. R. Crespo Lopez-Urrutia, C. Höhr, P. Neumayer, J. Ullrich, H. Rottke, C. Trump, M. Wittmann, G. Korn, and W. Sandner, *Phys. Rev. Lett.* **87**, 043003 (2001).
- [30] D. Comtois, D. Zeidler, H. Pépin, J. C. Kieffer, D. M. Villeneuve, and P. B. Corkum, *J. Phys. B* **38**, 1923 (2005).
- [31] M. Bashkansky, P. H. Bucksbaum, and D. W. Schumacher, *Phys. Rev. Lett.* **60**, 2458 (1988).
- [32] S. P. Goreslavski, G. G. Paulus, S. V. Popruzhenko, and N. I. Shvetsov-Shilovski, *Phys. Rev. Lett.* **93**, 233002 (2004).
- [33] K. Doblhoff-Dier, K. I. Dimitriou, André Staudte, and S. Gräfe, *Phys. Rev. A* **88**, 033411 (2013).
- [34] M. Spanner, S. Gräfe, S. Chelkowski, D. Pavičić, M. Meckel, D. Zeidler, A. B. Bardon, B. Ulrich, A. D. Bandrauk, D. M. Villeneuve, R. Dörner, P. B. Corkum, and A. Staudte, *J. Phys. B* **45**, 194011 (2012).
- [35] C. Huang, P. Lan, Y. Zhou, Q. Zhang, K. Liu, and P. Lu, arXiv:1401.0613v1.